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(54) Process for producing benzyl acetate and benzyl alcohol

Verfahren zur Herstellung von Benzylacetat und Benzylalkohol

Procédé de préparation d'acétate benzylique et d'alcool benzylique

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Description

[0001] The present invention relates to a process for producing benzyl acetate.

[0002] Benzyl acetate itself is useful as a solvent and a perfume. Benzyl alcohol which is derived from the benzyl acetate by hydrolysis or by transesterification with methanol is an important compound useful as a powerful solvent, a nontoxic medical additive, and an intermediate compound for agricultural chemicals and medicines.

[0003] For industrial production of benzyl acetate, a process is known in which benzyl chloride produced by chlorination of toluene is hydrolyzed by alkali, and the resulting benzyl alcohol is esterified with acetic acid. This process comprises multistage reactions, and includes many steps of separation and purification after the respective reactions. Therefore, the process is complex and is not advantageous economically. Moreover, in the hydrolysis reaction of the second step, an alkali such as sodium hydroxide is required in an equivalent amount or more, and a large amount of a salt containing organic compounds is formed as the by-product, which involves problems in after-treatment thereof.

[0004] In a process not industrially conducted, benzyl acetate is produced by reaction of toluene, acetic acid, and oxygen in the presence of a catalyst for oxyacetoxylation. This process produces benzyl acetate in an one step reaction without formation of a by-product salt, so that it is advantageous economically and can be of low environmental load.

[0005] Many techniques of benzyl acetate production have been disclosed, for example, in JP-B-42-13081, JP-A-52-151135, JP-A-52-151136, JP-B-50-28947, JP-B-52-16101, and JP-A-63-174950 (The term "JP-A" herein means an "unexamined published Japanese patent application", and the term "JP-B" herein means an "examined Japanese patent publication"). However, in these techniques, detailed studies are not made on industrial production process including separation and purification of benzyl acetate. Therefore, known techniques are not satisfactory for production of high-purity benzyl acetate.

[0006] On the other hand, benzyl alcohol can be produced by the known processes below. Of these, the processes (1) and (3) are practiced industrially:

(1) Hydrolysis of benzyl chloride by sodium hydroxide,
(2) Hydrolysis of benzyl acetate in the presence of a catalyst, and
(3) Reduction of benzaldehyde by hydrogen in the presence of a catalyst.

[0007] The above processes (1) and (2) both produces benzyl alcohol by hydrolysis. The process (1) consumes an equivalent amount or more of sodium hydroxide for stoichiometric reaction of benzyl chloride, involving a problem of after-treatment of a large amount of an aqueous solution of organic compound-containing sodium chloride formed as a by-product. The process (3) employs relatively expensive benzaldehyde as the starting material, and is disadvantageous economically.

[0008] The process (2) of hydrolysis of benzyl acetate to produce benzyl alcohol forms useful acetic acid as the by-product without discharging waste water, thus being economical and of low environmental load.

[0009] Regarding this hydrolysis process, a method is disclosed in which a mixture of water and benzyl acetate in a volume ratio of water/benzyl acetate of 25 is hydrolyzed at a temperature of 20-30°C in the presence of Amberlite IR-100, a sulfonic acid type cation-exchange resin (J. Chem. Soc., No.5, 1952, 1607). However, in this process, the catalyst activity is low, and an extremely large amount of water is required, so that the starting material concentration is lowered. Therefore, this process is not industrially advantageous in consideration of the energy for removal of unreacted water from the liquid reaction mixture. Further, the above disclosure does not specifically disclose the method for isolation and purification of the resulting benzyl alcohol.

[0010] In another process (Russian Patent: SU1077875), benzyl alcohol of high purity (98%) is obtained at an improved yield by hydrolysis of benzyl acetate in a flow system at a temperature of 90-98°C at water/benzyl acetate ratio of 3 (by weight) through a porous sulfonic acid type cation-exchange resin containing 2.2-4.0 m-equivalent/g of nitro group by replacing acetic acid with water during the reaction. However, this process, which requires use of a special nitro group-containing resin as the catalyst, is not practical as an industrial process in view of the catalyst cost.

[0011] As discussed above, the benzyl alcohol production process has not yet been investigated sufficiently for industrialization including the separation and purification steps, and no process is satisfactory as the process for producing high-purity benzyl alcohol.

[0012] An object of the present invention is to provide a process for economical production of benzyl acetate of high purity.

[0013] As a solution of the above-described problems, it has been found that benzyl acetate of high purity can be produced economically in an one step reaction of oxyacetoxylation by constructing a distillation purification process in consideration of the boiling points, the solubilities, and the azeotropy of the components including benzyl acetate as an oxyacetoxylation product, unreacted toluene and acetic acid, and recycling the process distillation fractions to the specified process, by use of a specific catalyst composed of an alloy of palladium and bismuth supported on silica, exhibiting high selectivity and having a long life.

[0014] Fig. 1 is a flow sheet showing specifically an example of a process of production of benzyl acetate of the present invention.

[0015] Fig. 2 is an XRD chart of the catalyst prepared in Example 2.

[0016] Fig. 3 is an XRD chart of the catalyst prepared in Comparative Example 1.

[0017] Fig. 4 is an XRD chart of the catalyst prepared in Comparative Example 2.

[0018] Fig. 5 is an XRD chart of the catalyst prepared in Comparative Example 3.

[0019] Fig. 6 is an XRD chart of the catalyst prepared in Comparative Example 4.

[0020] The process for production of benzyl acetate of the present invention is described below.

[0021] Toluene and acetic acid are employed as the starting materials in the process of the present invention.

[0022] The toluene and the acetic acid employed as the starting materials are not limited in the production processes thereof. For example, the toluene may be a product separated from petroleum distillate, or from cracked oil derived by cracking of petroleum distillate. The acetic acid may be a product obtained by oxidation of acetaldehyde, by oxidation of a hydrocarbon, or by synthesis from methanol and carbon monoxide.

[0023] In the process of the present invention, benzyl acetate is produced by oxyacetoxylation by use of toluene, acetic acid, and oxygen in a oxyacetoxylation reactor containing an oxyacetoxylation catalyst.

[0024] The oxyacetoxylation catalyst is not specially limited provided that it is capable of causing the intended oxyacetoxylation. For example, the catalysts are preferred which contain palladium having an oxyacetoxylation activity as the main component. Specifically, JP-B-42-13081 discloses a catalyst system comprising palladium supported by alumina and an alkali metal acetate. JP-A-52-151135 and JP-A-151136 disclose catalysts composed of a combination of one of bismuth, molybdenum, manganese, vanadium, and tungsten with palladium supported on silica. JP-B-50-28947 discloses a catalyst system comprising a catalyst composed of a combination of one of bismuth, cobalt, and iron with palladium supported on silica, and potassium acetate. JP-B-52-16101 discloses a catalyst system comprising a catalyst composed of palladium, bismuth, and chromium supported on silica, and an alkali metal acetate. JP-A-63-174950 discloses a catalyst system composed of palladium, and bismuth or lead supported on silica, and a bismuth compound or a lead compound soluble in the reaction system. In the present invention, any of the above catalysts can be used without difficulty. As the catalyst containing oxyacetoxylation-active palladium as a main component, another catalyst described later is useful which comprises an alloy composed of palladium and bismuth supported on silica at a palladium/bismuth ratio ranging from 2.5 to 3.5 (atomic ratio).

[0025] Such a catalyst is used as a fixed bed, a suspension catalyst bed and so on; in a reactor, a fixed bed is preferable. The amount of the catalyst depends on its activity, and is not generally specified. However, it corresponds preferably to the total feed of toluene and acetic acid per unit catalyst volume per unit time (LHSV) in the range of from 0.1 to 30 h^{-1} in consideration of production cost. The material of the reactor is not specially limited provided that it is sufficiently corrosion-resistant. For example, when stainless steel is used, SUS316 of JIS or higher corrosion-resistant grade of steel is preferred in consideration of the production cost.

[0026] For the oxyacetoxylation, a continuous fixed-bed flow reaction system is preferred in which the liquid starting materials of toluene and acetic acid and a prescribed concentration of oxygen are continuously fed in the reactor, and brought into contact with the fixed catalyst bed. The oxyacetoxylation reactor may be of a single-tubular type or a multitubular type, but is not limited thereto. The reaction proceeds by oxidation with generation of heat. The heat control method is not specially limited, and the reaction may be conducted with an adiabatic reaction system, with a multitubular reactor system with removal of the reaction heat, or with fractional material feed system.

[0027] The composition of the starting material liquid is generally in the range of from 0.1 to 10 moles of acetic acid per mole of toluene. However, when the catalyst employed comprises an alloy composed of palladium and bismuth supported on silica at a palladium/bismuth ratio ranging from 2.5 to 3.5 (atom ratio) as described later, the ratio of acetic acid is generally in the range of from 0.1 to 100, preferably from 0.2 to 40 moles per mole of toluene as mentioned later.

[0028] The oxidant employed in the present invention is molecular oxygen. The oxygen may be diluted with an inert gas such as nitrogen. In the practical process, air is preferably used.

[0029] The optimum feed rate of oxygen depends on the reaction conditions, the amount of the catalyst, and so forth, and is not generally limited. However, the feed should be controlled to give the total concentration of toluene, acetic acid and benzyl acetate outside the explosion range at least at the outlet portion of the oxyacetoxylation reactor. The feed rate of oxygen per unit catalyst volume per unit time (GHSV) is preferably not more than 5000 h^{-1} in terms of the volume at 0°C at 1 atmosphere.

[0030] The reaction according to the present invention is conducted usually under heated and pressurized conditions. The reaction temperature is preferably in the range of from 80 to 230°C, more preferably from 120 to 200°C. At a higher temperature, side reactions are promoted without advantage, whereas at a lower temperature, the reaction rate is low disadvantageously. The pressure is applied to maintain a liquid phase on the surface of the catalyst, and is generally in the range of from 0.4 to 9.9 MPa (3 to 100 kg/cm^2G), preferably from 0.6 to 5.0 MPa (5 to 50 kg/cm^2G). The reaction time is preferably in the range of from 0.03 to 10 hours as the liquid residence time in the reactor.

[0031] The effluent from the oxyacetoxylation reactor is introduced to a gas-liquid separator to separate the liquid phase and the gas phase.

[0032] By selecting the method of discharging the effluent from the outlet of the oxyacetoxylation reactor, the gas and the liquid can be separated without an extra independent gas-liquid separator. This reactor is regarded as an integrated reactor-separator, and may be employed in the present invention.

[0033] The liquid phase from the gas-liquid separator is a liquid mixture mainly composed of toluene, acetic acid, and benzyl acetate, and is introduced to a starting-material recovery column. In the starting-material recovery column, the liquid is subjected to distillation to recover a liquid mixture distillate composed mainly of unreacted toluene and unreacted acetic acid from the column top, and to obtain a liquid mixture mainly composed of benzyl acetate, the objective product, from the column bottom. The column top distillate, which is recovered from the starting-material recovery column and composed mainly of toluene and acetic acid, is recycled to the oxyacetoxylation reactor.

[0034] The bottom liquid recovered from the starting-material recovery column, with or without adjustment of the temperature and pressure, is fed to a low-boiler removal column. In the low-boiler removal column, distillation is conducted to separate a column top liquid mainly composed of benzaldehyde and a bottom liquid mainly composed of benzyl acetate. The distillation conditions for the low-boiler removal column is not specially limited, provided that components such as benzaldehyde having a lower boiling point than benzyl acetate can be removed from the column top.

[0035] The bottom liquid mainly composed of benzyl acetate recovered from the low-boiler removal column is, with or without adjustment of the temperature and pressure, introduced to a high-boiler removal column. In the high-boiler removal column, distillation is conducted to obtain benzyl acetate of acceptable product purity from the top of the column, and components such as benzoic acid and benzyl benzoate having a higher boiling point than benzyl acetate is removed from the bottom of the high-boiler removal column. The distillation conditions for the high-boiler removal column is not specially limited, and is selected depending on the required purity of the produced benzyl acetate. For higher quality of benzyl acetate, an additional distillation column may be employed for further distillation and purification.

[0036] The embodiments of the present invention are described more specifically by reference to drawings. The present invention includes various types of embodiments, and is not limited to the embodiment shown by the drawings.

[0037] In Fig. 1, an oxyacetoxylation reactor 1 is fed with toluene, acetic acid, and air as the starting materials, a recycled liquid phase portion mainly composed of toluene and acetic acid introduced from a starting-material recovery column 3 and a water removal column 7, and a recycled gas phase portion mainly composed of oxygen and nitrogen introduced at least from a condenser 6.

[0038] The manner of feeding the starting materials is not specially limited provided that the starting material liquid covers the surface of the catalyst to conduct the reaction in a liquid phase. The starting materials may be fed either in a gas-liquid concurrent system or in a gas-liquid countercurrent system of whether up stream or down stream. The starting liquid materials and/or air may be fed fractionally to the oxyacetoxylation reactor 1.

[0039] The gas-liquid mixed phase effluent from the oxyacetoxylation reactor 1 is fed to a gas-liquid separator 2.

[0040] The gas phase portion discharged from the gas-liquid separator 2 is introduced to a condenser 6 to separate the liquid phase mainly composed of toluene, acetic acid, and benzyl acetate from the gas phase mainly composed of oxygen and nitrogen.

[0041] At least a part of the liquid phase portion separated by the condenser 6 is mixed with the liquid portion from the gas-liquid separator 2, and the mixture is introduced to the starting-material recovery column 3, and the remainder of the liquid phase portion is fed to the water removal column 7. At least a part of the gas phase portion separated by the condenser 6 is recycled to the oxyacetoxylation reactor 1, and the remainder of the gas phase is purged to the outside of the system. The amount of the recycling part of the gas phase portion introduced to the oxyacetoxylation reactor 1 is controlled to give a desired oxygen concentration in the mixture with the fresh air introduced to the reactor 1.

[0042] Various condensing apparatuses and operation methods therefor are known, and are applicable to the process of the present invention. The condensation may be conducted in plural times. For example, a condensate containing a larger amount of high-boiling benzaldehyde and benzyl acetate is separated by a first condensation; the separated condensate is fed to the starting-material recovery column 3; the remaining gas phase portion is subjected to a second condensation to remove a condensate composed mainly of toluene, acetic acid, and water; and the -condensate is fed to the water removal column 7.

[0043] By this method, the load to the starting-material recovery column 3 is reduced; the recycling amount of benzyl acetate to the oxyacetoxylation reactor 1 is reduced to improve the reaction yield of the intended benzyl acetate; and further, the recycling amount of by-product benzaldehyde to the oxyacetoxylation reactor 1 is reduced, advantageously.

[0044] Most of the liquid phase portion introduced from the condenser 6 to the water removal column 7 is composed mainly of toluene, acetic acid, and water, and is subjected to distillation in the water removal column 7 to obtain a column top distillate mainly composed of toluene and water as the main distillate fraction. This column top distillate mainly composed of toluene and water is separated into two liquid phases in a settling vessel 8, and the upper phase mainly composed of toluene is recycled without treatment to the oxyacetoxylation reactor 1, and the lower phase mainly composed of water is eliminated. From the bottom of the water removal column 7, acetic acid is obtained, which is

recycled without treatment to the oxyacetoxylation reactor 1.

[0045] The liquid phase portion from the gas-liquid separator 2 is mixed with a part or the whole of the liquid phase separated by the condenser 6, and the mixture is introduced to the starting-material recovery column 3. This liquid mixture contains a non-condensable gas component such as oxygen and nitrogen dissolved therein, so that the dissolved non-condensable gas is preferably eliminated prior to introduction to the starting-material recovery column 3 by a known apparatus and operation such as a flash evaporator and a vacuum deaerator. This method enables miniaturization of the starting-material recovery column 3, and makes unnecessary an extra device and operation for reducing the loss of useful component by discharge of the non-condensable gas.

[0046] The column top distillate of the starting-material recovery column 3, which is mainly composed of toluene and acetic acid is recycled without treatment to the oxyacetoxylation reactor 1.

[0047] In the process of the present invention, the recycled liquid phase portion mainly composed of toluene and acetic acid introduced to the oxyacetoxylation reactor 1 contains a small amount of water. A high concentration of water therein can adversely affect the activity and selectivity of the catalyst. Therefore, in order to prevent increase of the water concentration, the gas-liquid separation conditions in the gas-liquid separator 2, the condensation conditions in the condenser 6, and the distillation conditions in the starting-material recovery column 3 and the water removal column 7 are preferably controlled such that the water concentration is kept to be not more than 5% by weight in the entire liquid mixture of the toluene and the acetic acid supplied to the oxyacetoxylation reactor 1 and the recycled liquid phase portion mainly composed of toluene and acetic acid.

[0048] As described above, according to the present invention, benzyl acetate of high purity can be produced at a low cost through one step of oxyacetoxylation reaction of toluene, acetic acid, and oxygen and separation from the resulting mixture of the reaction products including benzyl acetate and water and unreacted materials including toluene and acetic acid.

[0049] The efficient combination of the gas-liquid separation operation and the condensation operation facilitates recovery and purification of the unreacted materials contained in the gas-liquid mixture effluent from the reactor, reduces the load to the starting-material recovery column, reduces the equipment cost, and saves energy, which is greatly advantageous economically and industrially.

[0050] The specific catalyst employed in the present invention is described below.

[0051] In the present invention, benzyl acetate is produced by reaction of toluene, acetic acid, and molecular oxygen in a liquid phase in the presence of a catalyst constituted of an alloy supported on silica, the alloy comprising palladium and bismuth in a palladium/bismuth ratio in the range of from 2.5 to 3.5 (atomic ratio).

[0052] The silica for the catalyst in the present invention is not specially limited, and may be any silica regardless of the raw material and production process therefor. However, the silica has preferably properties of the BET specific surface area of not less than 10 m^2/g, and the pore volume of not less than 0.2 cc/g.

[0053] The shape of the catalyst is not limited specially, and may be in a form of a powder, tablet or sphere shape. For a suspension catalyst bed, the catalyst is preferably powdery or granular, and for a fixed catalyst bed, the catalyst is preferably in a form of a molded article such as tablets, sphere shape and extrusion molded articles of a column shape.

[0054] The raw materials for palladium and bismuth for preparation of the catalyst employed in the present invention is not specially limited provided that the palladium and the bismuth can finally be alloyed.

[0055] Specifically, the raw material for the palladium includes metallic palladium, ammonium hexachloropalladate, potassium hexachloropalladate, ammonium tetrachloropalladate, potassium tetrachloropalladate, sodium tetrachloropalladate, potassium tetrabromopalladate, palladium oxide, palladium chloride, palladium bromide, palladium iodide, palladium nitrate, palladium sulfate, palladium acetate, potassium dinitrosulfitepalladate, chlorocarbonylpalladium, dinitrodiamminepalladium, tetraamminepalladium chloride, tetraamminepalladium nitrate, cis-dichlorodiamminepalladium, trans-dichlorodiamminepalladium, dichloro(ethylenediamine)palladium, potassium tetracyanopalladate, and the like. The raw material for the bismuth includes metallic bismuth, bismuth chloride, bismuth nitrate, bismuth oxychloride, bismuth acetate, bismuth oxyacetate, bismuth oxide, and the like.

[0056] The amount of the supported metal of the catalyst is usually in the range of from 0.1 to 10% by weight based on the total catalyst weight including the supporting silica as an alloy consisting of palladium and bismuth in a palladium/bismuth ratio of from 2.5 to 3.5 (atomic ratio).

[0057] The palladium supported by silica should substantially be in a state of an alloy, although excess bismuth may exist in the catalyst without forming the alloy in the present invention.

[0058] The palladium substantially in a state of a palladium-bismuth alloy can be confirmed by measuring adsorption of carbon monoxide onto the catalyst, because the palladium-bismuth alloy does not adsorb carbon monoxide. Thus, palladium in a non-alloy state adsorbs carbon monoxide, and can be readily distinguished from the alloy.

[0059] The palladium-bismuth alloy of a palladium/bismuth ratio ranging from 2.5 to 3.5 (atomic ratio) shows a characteristic X ray diffraction pattern at 2θ ranging from 30 to 80° as shown in Table 1.

[0060] This alloy will not change its X-ray diffraction pattern even when it is heated to 400°C in a nitrogen atmosphere, or to 200°C in the air. If the particle size of the alloy is too small for peak assignment in the X-ray diffraction pattern,

the applicability of the catalyst to the process of the present invention can be confirmed by analysis by combination of high-resolution electron microscopy with electron beam diffraction or X-ray fluorescence.

[0061] In preparation of the catalyst constituted of the alloy supported on silica, the palladium-bismuth alloy of palladium/bismuth ratio of 2.5-3.5 (atomic ratio) of the present invention, the starting material for the palladium and the bismuth may be deposited by any known method in which palladium and bismuth form the alloy. Specifically the method includes precipitation, ion-exchange, immersion, deposition, blending, and so forth.

[0062] In catalyst preparation by immersion, the method of impregnation is not specially limited provided that the palladium and the bismuth finally form an alloy. A palladium material and a bismuth material may be impregnated simultaneously, or successively. For forming a more uniform alloy, the simultaneous impregnation is preferred. In a specific example of the simplest preparation method of the catalyst of the present invention, materials for the palladium and the bismuth are dissolved in a suitable solvent (the starting material salts for palladium and bismuth being preferably mixed in a palladium/bismuth ratio ranging from 2.5 to 3.5 (atomic ratio)); the solution is mixed with silica; the mixture is kept standing for a prescribed time as necessary, and is dried; and the resulting catalyst precursor is reduced in a hydrogen atmosphere or a hydrogen-containing inert gas atmosphere. Before the reduction treatment with hydrogen, the catalyst precursor may be calcined in an oxygen atmosphere.

[0063] The reduction treatment is conducted at a temperature ranging usually from 100 to 700°C, preferably from 200 to 500°C. The reducing agent for the reduction treatment includes gases such as hydrogen, carbon monoxide, and ethylene, alcohols, and hydrazine hydrate. The reduction treatment may be conducted in a gas phase or in a liquid phase.

[0064] The calcination before the reduction treatment, if necessary, is conducted in an oxygen atmosphere, in an atmosphere of oxygen diluted with nitrogen, helium, argon or the like, or in the air at a temperature ranging usually from 200 to 700°C.

[0065] The toluene and acetic acid used as the starting materials in the present invention are not limited in their production process. For example, the toluene may be a product separated from petroleum distillate, or from cracked oil derived by cracking of petroleum distillate. The acetic acid may be a product produced by oxidation of acetaldehyde, produced by oxidation of a hydrocarbon, separated from a by-product in peracetic acid, or synthesized from methanol and carbon monoxide. The mixing ratio of toluene to acetic acid is selected as desired in the range of from 0.1 to 100 moles, preferably from 0.2 to 40 moles per mole of toluene.

[0066] The reaction may be conducted in the present invention by dissolving a soluble bismuth compound in toluene and/or acetic acid. In this case, the amount of the soluble bismuth compound dissolved in toluene and/or acetic acid is preferably in the range shown by the equation below:

$$1 \times 10^{-9} \leq \frac{\text{(Weight of Bismuth as Metal)}}{\text{(Weight of Toluene + Acetic Acid)}} \leq 1 \times 10^{-5}$$

[0067] The catalyst employed in the present invention is stable in the reaction system. Therefore, the co-existence of the soluble bismuth compound is not essential. The amount of the co-existing soluble bismuth compound is sufficient in the range shown above. The soluble bismuth compound in an amount much larger than that shown above, may deposit in the process of purification of the produced benzyl acetate to clog pipe lines.

[0068] The soluble bismuth compound includes bismuth nitrate, bismuth oxide, bismuth oxyacetate, bismuth hydroxide, bismuth chloride, bismuth oxychloride, basic bismuth carbonate, bismuth acetate, bismuth oxalate, and trimethylbismuth, but is not limited thereto.

[0069] The reaction is conducted in a liquid phase in the present invention. The method of the reaction is not specially limited provided that the surface of the catalyst is covered with the starting material liquid. The reaction may be conducted by a batch process, a semi-batch process, a continuous process, or may be conducted with a reactor of fixed-bed flow or suspension system. The catalyst of the present invention may be applied to the aforementioned oxyacetoxylation process.

[0070] The amount of the catalyst depends on the method of the reaction, and is not defined generally. However, in consideration of the production cost, the amount of the catalyst in a fixed bed process is such that the total feed of toluene and acetic acid per unit volume of the catalyst per unit time (LHSV) in a fixed bed is in the range of preferably from 0.1 to 50 h^{-1}, more preferably from 0.1 to 30 h^{-1}, and in a suspension bed, the concentration of the catalyst is preferably in the range of from 0.1 to 30% by weight as the starting materials.

[0071] The oxygen partial pressure in the gas phase in the reactor is preferably controlled in the range of from 0.01 to 0.2 MPa (0.1 to 2 kg/cm^2) for maintaining the catalyst life by securing activity and selectivity of the catalyst in the present invention from industrial standpoint. At the oxygen partial pressure of lower than 0.01 MPa (0.1 kg/cm^2), the activity is not sufficient industrially, whereas at the partial pressure of higher than 0.2 MPa (2 kg/cm^2), elution of palladium may be promoted to deteriorate remarkably the catalyst activity. The feed rate of oxygen is preferably in the range of from 0.5 to 4.5 moles per hour per one liter of catalyst. Incidentally, the reactor in the present invention means

a vessel, a column, or a tube for synthesis of benzyl acetate by reaction of toluene, acetic acid, and oxygen as the starting materials, including specifically reaction vessels having a suspension bed, a catalyst-packed column or multi-tubular reactor having a fixed bed, etc.

[0072] The reaction according to the present invention is conducted usually in a heated and pressurized state. The reaction temperature is in the range of usually from 80 to 230°C, preferably from 120 to 200°C. At a higher reaction temperature than that range, side reactions are promoted without advantage, whereas at a lower temperature, reaction rate is lower disadvantageously. The reaction pressure is not limited specially provided that the liquid phase is maintained on the catalyst surface at the reaction temperature, and is in the range usually of from 0.4 to 9.9 MPa (3 to 100 kg/cm^{2}G), preferably from 0.5 to 5.0 MPa (4 to 50 kg/cm^{2}G). The reaction pressure higher than that is not necessary, since the intended reaction proceeds satisfactorily in the above pressure range.

[0073] The oxidizing agent in the process of the present invention is oxygen. The oxygen may be diluted with an inert gas such as nitrogen, or the oxidizing agent may be air. The optimum feed rate of the oxygen depends on the reaction temperature, the amount of the catalyst, and so forth, and the gas composition is controlled to be outside the explosion range at the outlet portion of the reacter. The feed rate of oxygen per unit catalyst amount per unit time (GHSV) is preferably not higher than 5000 h^{-1} in terms of the rate at 0°C, and 1 atmosphere.

[0074] The reaction time depends on the reaction temperature, the reaction pressure, the catalyst amount, and other conditions, and cannot be defined generally. In a batch or semi-batch system with a suspension catalyst bed, the reaction time is not shorter than 0.5 hour, and preferably in the range of from 1 to 10 hours. In a continuous system with a suspension catalyst bed, or in a flow system with a fixed catalyst bed, the residence time is generally in the range of from 0.03 to 10 hours.

[0075] As described above, according to the present invention, industrially useful benzyl acetate can be produced by liquid phase reaction of toluene, acetic acid, and molecular oxygen, by employing a catalyst comprising a specific composition of palladium and bismuth supported on silica, with a high catalyst activity, a high selectivity, and long life of the catalyst.

[0076] Furthermore, the benzyl acetate synthesis can be continued for a long term with retention of industrially satisfactory activity and selectivity by controlling the oxygen partial pressure in the gas phase to be within the specified range, and by controlling the feed rate of oxygen to the catalyst to be within the specified range.

[0077] The present invention is described in more detail by reference to examples.

[0078] In the description below, "%" is based on weight, and benzyl acetate is denoted by "BzOAc".

Example 1

[0079] This Example is explained by reference to Fig. 1.

[0080] An oxyacetoxylation reactor 1 was packed with 100 mL of a catalyst composed of a palladium-bismuth catalyst supported on spherical silica. To the reactor 1, were fed a liquid starting material composed of toluene, acetic acid, and recycling liquid recovered by distillation separation by a starting material recovery column 3 and a water removal column 7 (toluene: 59.7%, acetic acid 39.0%, and water: 1.2%) at a rate of 200.5 g/h; and air at a rate of 14.4 g/h and a recycling gas at a rate of 9.9 g/h (oxygen: 3.9%, and nitrogen: 92.6%) as the starting gas material, at a catalyst layer inlet temperature of 170°C and a pressure of 1.5 MPa (14 kg/cm^{2}G) to cause reaction.

[0081] As the results, 224.8 g/h of gas-liquid mixture effluent was obtained (composed of toluene: 47.4%, acetic acid: 31.4%, benzyl acetate: 8.3%, water: 2.2%, benzaldehyde: 0.3%, benzoic acid: 0.6%, benzyl benzoate: 0.2%, oxygen: 0.3%, and nitrogen: 9.0%). The temperature of the reactor outlet was 190°C.

[0082] The gas-liquid mixture effluent was introduced to a gas-liquid separator 2 to separate the gas and the liquid. The gas phase portion was partially condensed, and the condensate was combined with the liquid phase portion. The liquid phase portion was flash-evaporated at an atmospheric pressure. The generated vapor was condensed by cooling to 98°C to obtain a condensate, and the condensate was combined with the liquid phase obtained by the flash-evaporation. Thus 117.2 g/h of a liquid effluent was obtained (the liquid composed of toluene: 46.2%, acetic acid: 36.1%, benzyl acetate: 15.2%, water: 0.3%, benzaldehyde: 0.6%, benzoic acid: 1.1%, and benzyl benzoate: 0.4%).

[0083] The liquid effluent was continuously introduced to a starting material recovery column 3 at a column top pressure of 17.3 kPa (130 Torr) to obtain 95.6 g/h of a column top distillate (composed of toluene: 56.1%, acetic acid: 43.6%, and water: 0.4%), and 21.6 g/h of a column bottom liquid (composed of acetic acid: 1.4%, benzyl acetate: 86.0%, benzaldehyde: 3.2%, benzoic acid: 6.5%, and benzyl benzoate: 2.3%).

[0084] The bottom liquid of the starting material recovery column 3 was held temporarily in a vessel, and introduced to a low-boiler removal column 4 at a column top pressure of 5.3 kPa (40 Torr) continuously at a rate of 107.9 g/h to obtain 4.3 g/h of a column top distillate (composed of toluene: 1.7%, acetic acid: 20.9%, and benzaldehyde: 77.3%), and 103.6 g/h of a column bottom liquid (benzyl acetate: 90.2%, benzoic acid: 6.8%, and benzyl benzoate: 2.4%).

[0085] Further, the column bottom liquid of the low-boiler removal column 4 was introduced continuously to a high-boiler removal column 5 at a column top pressure of 2.7 kPa (20 Torr) to obtain 93.3 g/h of benzyl acetate having a

purity of 99.8% from the column top.

Example 2

[0086] In a 200-mL round-bottomed flask, were placed 2.00 g (11.28 mmol) of palladium chloride (Wako Pure Chemical Industries, Ltd.) and 1.18 g (3.75 mmol) of bismuth chloride (Wako Pure Chemical Industries, Ltd.). Thereto, 43 mL of 6N hydrochloric acid was added, and the content in the flask was stirred at a room temperature until the palladium chloride and the bismuth chloride came to be completely dissolved. The atomic ratio of palladium and bismuth used was 3.0.

[0087] There, 40 g of silica (CARIACT-Q30, Fuji Silicia K.K.) having been dried at 180°C for 2 hours (BET surface area: 100 m^2/g, pore volume: 1.05 cc/g, sphere shape of 3 mm diameter) was added, and the solution in the flask was impregnated into the silica by stirring the mixture until the liquid came to be completely absorbed.

[0088] After the impregnation, the water was removed under a reduced pressure by a rotary evaporator.

[0089] The obtained catalyst precursor was place in a heat-treatment tube, and treated for reduction by hydrogen gas flow of 50 mL/min at 400°C for 5 hours.

[0090] The catalyst after the reduction treatment was washed with deionized water repeatedly until the chloride ion came to be not detected by the mercuric thiocyanate method. The washed catalyst was dried at 110°C for 3 hours.

[0091] The obtained catalyst was analyzed by X-ray diffraction and was found that a palladium-bismuth alloy was formed in a palladium/bismuth atomic ratio of 3 as shown in Fig. 2.

[0092] This catalyst (10 cc) was mixed with 10 cc of glass beads of 1 mm diameter, and the mixture was packed in a SUS316 reaction tube of 13 mm inside diameter. Thereto, toluene (19.5 g/h), acetic acid (80.5 g/h), and oxygen (21 NmL/min), and nitrogen (79 NmL/min) were continuously fed to react at a reaction temperature of 150°C at a pressure of 0.5 MPa (4 kg/cm^2G).

[0093] The reaction product was separated into a liquid and a gas. The liquid component and the gas component were respectively analyzed by gas chromatography.

[0094] At the time after 5 hours from the start of the reaction, the space time yield of benzyl acetate (STY: produced amount of benzyl acetate per unit volume of catalyst per unit time) was 165 g/h/L and the selectivity was 98% for acetic acid.

[0095] From the general equation (7) below for catalyst deterioration, the time for dropping the STY of benzyl acetate by half was calculated to be about 1000 hours.

$$Ln(r/r0) = -kt \quad (7)$$

where r is an STY of benzyl acetate at a time t, r0 is an initial STY of benzyl acetate, and k is a catalyst deterioration constant.

[0096] A CO adsorption amount and a Pd elution rate at 50 hours after the start of the reaction is shown in Table 3.

Comparative Example 1

[0097] In a 200-mL round-bottomed flask, were placed 2.00 g (11.28 mmol) of palladium chloride (Wako Pure Chemical Industries, Ltd.) and 3.56 g (11.28 mmol) of bismuth chloride (Wako Pure Chemical Industries, Ltd.). Thereto, 43 mL of 12N hydrochloric acid was added, and the content in the flask was stirred at a room temperature until the palladium chloride and the bismuth chloride came to be completely dissolved.

[0098] There, 40 g of silica (CARIACT-Q30, Fuji Silicia K.K.) having been dried at 180°C for 2 hours (BET surface area: 100 m^2/g, pore volume: 1.05 cc/g, sphere shape of 3 mm diameter) was added, and the solution in the flask was impregnated into the silica by stirring the mixture until the liquid came to be completely absorbed.

[0099] After the impregnation, the water was removed under a reduced pressure by a rotary evaporator.

[0100] The obtained catalyst precursor was placed in a heat-treatment tube, and treated for reduction by hydrogen gas flow of 50 mL/min at 400°C for 5 hours.

[0101] The catalyst after the reduction treatment was washed with deionized water repeatedly until the chloride ion came to be not detected by the mercuric thiocyanate method. The washed catalyst was dried at 110°C for 3 hours.

[0102] The obtained catalyst was analyzed by X-ray diffraction, and was found to be different from that obtained by Example 2 of the present invention as shown in Fig. 3.

[0103] The reaction and the analysis were conducted in the same manner as in Example 2 except that the above catalyst was used. The results are shown in Table 3.

Comparative Example 2

[0104] To 5.48 g (11.30 mmol) of bismuth nitrate pentahydrate (Wako Pure Chemical Industries, Ltd.), 43 mL of aqueous 7% nitric acid was added, and the bismuth nitrate pentahydrate was completely dissolved.

[0105] Thereto, 40 g of silica (CARIACT-Q30, Fuji Silicia K.K.) having been dried at 180°C for 2 hours (BET surface area: 100 m^2/g, pore volume: 1.05 cc/g, sphere shape of 3 mm diameter) was added, and the solution in the flask was impregnated into the silica by stirring the mixture until the liquid came to be completely absorbed.

[0106] After the impregnation, the water was removed under a reduced pressure by a rotary evaporator.

[0107] The obtained catalyst precursor was placed in a heat-treatment tube, and was calcined with a flow of air at a flow rate of 100 mL/min at 200°C for 2 hours to obtain a silica-supported bismuth catalyst.

[0108] Separately, 1.90 g (10.71 mmol) of palladium chloride (Wako Pure Chemical Industries, Ltd.) was dissolved in 43 mL of 3N hydrochloric acid. Thereto the above silica-supported bismuth catalyst was added, and the solution was impregnated into the silica by stirring the mixture until the liquid came to be completely absorbed. After the impregnation, the water was removed under a reduced pressure by a rotary evaporator.

[0109] The obtained catalyst precursor was placed in a heat-treatment tube, and was dried with a flow of nitrogen at a flow rate of 100 mL/min at 150°C for 2 hours. When the temperature of the catalyst layer dropped to a room temperature, the gas was changed to hydrogen at a flow rate of 50 mL/min to treat the catalyst precursor for reduction at 200°C for 2 hours, and at 400°C for 4 hours.

[0110] The catalyst after the reduction treatment was washed with deionized water repeatedly until the chloride ion came to be not detected by the mercuric thiocyanate method. The washed catalyst was dried at 110°C for 3 hours.

[0111] The obtained catalyst was analyzed by X-ray diffraction, and was found to be different from that obtained by Example 2 of the present invention as shown in Fig. 4.

[0112] The reaction and the analysis were conducted in . the same manner as in Example 2 except that the above catalyst was used. The results are shown in Table 3.

Comparative Example 3

[0113] To 2.74 g (5.65 mmol) of bismuth nitrate pentahydrate (Wako Pure Chemical Industries, Ltd.), 43 mL of aqueous 7% nitric acid solution was added, and the bismuth nitrate pentahydrate was completely dissolved.

[0114] Thereto, 40 g of silica (CARIACT-Q30, Fuji Silicia K.K.) having been dried at 180°C for 2 hours (BET surface area: 100 m^2/g, pore volume: 1.05 cc/g, sphere shape of 3 mm diameter) was added, and the solution was impregnated into the silica by stirring the mixture until the liquid came to be completely absorbed.

[0115] After the impregnation, the water was removed under a reduced pressure by a rotary evaporator. The solid matter was dried at 110°C for 3 hours to obtain silica-supported bismuth nitrate.

[0116] Separately, 2.53 g (11.29 mmol) of palladium acetate (Wako Pure Chemical Industries, Ltd.) was dissolved in 43 mL of aqueous 3.5% ammonia solution. Thereto the above silica-supported bismuth nitrate was added, and the solution was impregnated into the silica by stirring the mixture until the liquid came to be completely absorbed. After the impregnation, the water was removed under a reduced pressure by a rotary evaporator.

[0117] The obtained catalyst precursor was placed in a heat-treatment tube, and was treated for reduction by hydrogen flow of 50 mL/min at 400°C for 5 hours.

[0118] The obtained catalyst was analyzed by X-ray diffraction, and was found to be different from that obtained by Example 2 of the present invention as shown in Fig. 5.

[0119] The reaction and the analysis were conducted in the same manner as in Example 2 except that the above catalyst was used. The results are shown in Table 3.

Comparative Example 4

[0120] In a 200-mL round-bottomed flask, were placed 2.00 g (11.28 mmol) of palladium chloride (Wako Pure Chemical Industries, Ltd.) and 0.36 g (1.14 mmol) of bismuth chloride (Wako Pure Chemical Industries, Ltd.). Thereto, 43 mL of 6N hydrochloric acid was added, and the content in the flask was stirred at a room temperature to dissolve completely the palladium chloride and the bismuth chloride.

[0121] Thereto, 40 g of silica (CARIACT-Q30, Fuji Silicia K.K.) having been dried at 180°C for 2 hours (BET surface area: 100 m^2/g, pore volume: 1.05 cc/g, sphere shape of 3 mm diameter) was added, and the solution in the flask was impregnated into the silica by stirring the mixture until the liquid came to be completely absorbed. After the impregnation, the water was removed under a reduced pressure by a rotary evaporator.

[0122] The obtained catalyst precursor was place in a heat-treatment tube, and treated for reduction by hydrogen gas flow of 50 mL/min at 400°C for 5 hours.

[0123] The catalyst after the reduction treatment was washed with deionized water repeatedly until the chloride ion

came to be not detected by the mercuric thiocyanate method. The washed catalyst was dried at 110°C for 3 hours.

[0124] The obtained catalyst was analyzed by X-ray diffraction and was found that the X-ray diffraction pattern had peaks of Pd metal in addition to the peaks of the palladium-bismuth alloy of a palladium/bismuth atomic ratio of 3 as shown in Fig. 6, which is different from the catalyst obtained by Example 2 of the present invention.

[0125] The reaction and the analysis were conducted in the same manner as in Example 2 except that the above catalyst was used. The results are shown in Table 3.

Comparative Example 5

[0126] In a 200-mL round-bottomed flask, were placed 2.00 g (11.28 mmol) of palladium chloride (Wako Pure Chemical Industries, Ltd.). Thereto, 43 mL of 6N hydrochloric acid was added, and the content in the flask was stirred at a room temperature to dissolve completely the palladium chloride.

[0127] Thereto, 40 g of silica (CARIACT-Q30, Fuji Silicia K.K.) having been dried at 180°C for 2 hours (BET surface area: 100 m^2/g, pore volume: 1.05 cc/g, sphere shape of 3 mm diameter) was added, and the solution in the flask was impregnated into the silica by stirring the mixture until the liquid came to be completely absorbed. Thereafter, the catalyst preparation was conducted in the same manner as in Example 2.

[0128] The reaction and the analysis were conducted in the same manner as in Example 2 except that the above catalyst was used. The results are shown in Table 3.

Comparative Example 6

[0129] In a 200-mL round-bottomed flask, were placed 1.18 g (3.74 mmol) of bismuth chloride (Wako Pure Chemical Industries, Ltd.). Thereto, 43 mL of 6N hydrochloric acid was added, and the content in the flask was stirred at a room temperature to dissolve completely the palladium chloride. Thereafter, the catalyst preparation was conducted in the same manner as in Example 2.

[0130] The reaction and the analysis were conducted in the same manner as in Example 2 except that the above catalyst was used. As the results, no benzyl acetate was found to be formed.

Example 3

[0131] Ten milliliters of the catalyst prepared in Example 2 was packed in a SUS316 reaction tube of 13 mm inside diameter. Thereto, toluene (2.2 g/min), acetic acid (1.4 g/min), oxygen (23.3 NmL/min), and nitrogen (396 NmL/min) were continuously fed to react at a reaction temperature of 170°C at a pressure of 1.5 MPa (14 kg/cm^2G). During the reaction, the oxygen partial pressure was 0.06 MPa (0.6 kg/cm^2) in the gas phase in the reactor.

[0132] The reaction product was separated into liquid and a gas. The liquid component and the gas component were respectively analyzed by gas chromatography.

[0133] At a time after 3 hours from the start of the reaction, the space time yield STY of benzyl acetate was 313 g/h/L and the selectivity was 98% for acetic acid.

[0134] No elution of palladium into the reaction liquid was found by measurement by flameless atomic absorption spectrometry.

Comparative Example 7

[0135] The reaction and the product analysis were conducted in the same manner as in Example 3 except that the same lot of the catalyst prepared in Comparative Example 5 was used. The results are shown collectively in Table 4.

Example 4

[0136] The reaction and the product analysis were conducted in the same manner as in Example 3 except that the same lot of the catalyst prepared in Example 2 was used, and the continuous material feed rates were changed to toluene: 2.2 g/min, acetic acid: 1.4 g/min, oxygen: 38.5 NmL/min, and nitrogen: 381 NmL/min (the oxygen partial pressure: 0.1 MPa (1.0 kg/cm^2) in the gas phase in the reaction system). The results are shown collectively in Table 4.

Example 5

[0137] The reaction and the product analysis were conducted in the same manner as in Example 3 except that the same lot of the catalyst prepared in Example 2 was used, and the continuous material feed rates were changed to toluene: 2.2 g/min, acetic acid: 1.4 g/min, oxygen: 58.3 NmL/min, and nitrogen: 361 NmL/min (the oxygen partial pres-

sure: 0.15 MPa (1.5 kg/cm^2) in the gas phase in the reaction system). The results are shown collectively in Table 4.

Example 6

[0138] The reaction and the product analysis were conducted in the same manner as in Example 3 except that the same lot of the catalyst prepared in Example 2 was used, and the continuous material feed rates were changed to toluene: 2.8 g/min, acetic acid: 1.8 g/min, oxygen: 58.3 NmL/min, and nitrogen: 990 NmL/min (the oxygen partial pressure: 0.06 MPa (0.6 kg/cm^2) in the gas phase in the reaction system). The results are shown collectively in Table 4.

Example 7

[0139] The reaction and the product analysis were conducted in the same manner as in Example 3 except that the same lot of the catalyst prepared in Example 2 was used, and the continuous material feed rates were changed to toluene: 2.2 g/min, acetic acid: 1.4 g/min, oxygen: 87.5 NmL/min, and nitrogen: 332 NmL/min (the oxygen partial pressure: 0.22 MPa (2.25 kg/cm^2) in the gas phase in the reaction system). The results are shown collectively in Table 4.

Example 8

[0140] The reaction and the product analysis were conducted in the same manner as in Example 3 except that the same lot of the catalyst prepared in Example 2 was used, and the continuous material feed rates were changed to toluene: 2.2 g/min, acetic acid: 1.4 g/min, oxygen: 117 NmL/min, and nitrogen: 303 NmL/min (the oxygen partial pressure: 0.3 MPa (3.0 kg/cm^2) in the gas phase in the reaction system). The results are shown collectively in Table 4.

Example 9

[0141] Ten milliliters of the catalyst prepared in Example 2 and 10 mL of glass beads of 1 mm diameter were mixed, and was packed in a SUS316 reaction tube of 13 mm inside diameter. Thereto, toluene (0.14 g/min), acetic acid (0.1 g/min), oxygen (2.7 NmL/min: 0.7 mol/h per liter of catalyst), and nitrogen (209 NmL/min) were continuously fed to allow the reaction to proceed at a temperature of 170°C at a pressure of 4.4 MPa (44 kg/cm^{2}G).

[0142] The reaction product was separated into a liquid and a gas. The liquid component and the gas component were respectively analyzed by gas chromatography.

[0143] At a time after 20 hours from the start of the reaction, the time space yield STY of benzyl acetate was 83 g/h/L and the selectivity was 95% for acetic acid.

[0144] According to the general equation (7) of catalyst deterioration, the time for dropping the STY of benzyl acetate by half was calculated to be more than 10000 hours.

Example 10

[0145] The reaction and the product analysis were conducted in the same manner as in Example 9 except that the same lot of the catalyst prepared in Example 2 was used, and the continuous material feed rates were changed to toluene: 0.14 g/min, acetic acid: 0.1 g/min, oxygen: 7.8 NmL/min (2.1 mol/h per liter of catalyst), and nitrogen: 204 NmL/min. The results are shown collectively in Table 5.

Example 11

[0146] The reaction and the product analysis were conducted in the same manner as in Example 9 except that the same lot of the catalyst prepared in Example 2 was used, and the continuous material feed rates were changed to toluene: 0.14 g/min, acetic acid: 0.1 g/min, oxygen: 15.6 NmL/min (4.2 mol/h per liter of catalyst), and nitrogen: 196 NmL/min. The results are shown collectively in Table 5.

Example 12

[0147] The reaction and the product analysis were conducted in the same manner as in Example 9 except that the same lot of the catalyst prepared in Example 2 was used, the reaction pressure was changed to 1.5 MPa (14 kg/cm^{2}G), and the continuous material feed rates were changed to toluene: 0.3 g/min, acetic acid: 0.2 g/min, oxygen: 5.8 NmL/min (1.6 mol/h per liter of catalyst), and nitrogen: 51 NmL/min. The results are shown collectively in Table 5.

Example 13

[0148] The reaction and the product analysis were conducted in the same manner as in Example 8 except that the same lot of the catalyst prepared in Example 2 was used, and the continuous material feed rates were changed to toluene: 0.14 g/min, acetic acid: 0.1 g/min, oxygen: 20.7 NmL/min (5.5 mol/h per liter of catalyst), and nitrogen: 191 NmL/min. The results are shown collectively in Table 5.

Example 14

[0149] The reaction and the product analysis were conducted in the same manner as in Example 9 except that the same lot of the catalyst prepared in Example 2 was used, and the continuous material feed rates were changed to toluene: 0.14 g/min, acetic acid: 0.1 g/min, oxygen: 1.5 NmL/min (0.4 mol/h per liter of catalyst), and nitrogen: 210 NmL/min. The results are shown collectively in Table 5.

Example 15

[0150] The reaction and the product analysis were conducted in the same manner as in Example 3 except that the feed rates of toluene and acetic acid are changed to toluene: 3.1 g/min, and acetic acid: 0.4 g/min (ratio of acetic acid/toluene = 0.25 (mole ratio)). The results are shown in Table 6.

Example 16

[0151] The reaction and the product analysis were conducted in the same manner as in Example 3 except that the feed rates of toluene and acetic acid are changed to toluene: 1.0 g/min, and acetic acid: 2.7 g/min (ratio of acetic acid/toluene = 4 (mole ratio)). The results are shown collectively in Table 6.

Example 17

[0152] The reaction and the product analysis were conducted in the same manner as in Example 3 except that the feed rates of toluene and acetic acid are changed to toluene: 3.4 g/min, and acetic acid: 0.2 g/min (ratio of acetic acid/toluene = 0.11 (mole ratio)). The results are shown collectively in Table 6.

Example 18

[0153] The reaction and the product analysis were conducted in the same manner as in Example 3 except that the feed rates of toluene and acetic acid are changed to toluene: 0.1 g/min, and acetic acid: 3.6 g/min (ratio of acetic acid/toluene = 49 (mole ratio)). The results are shown collectively in Table 6.

Example 19

[0154] Into a SUS316 reaction tube of inside diameter of 13 mm, was packed 10 cc of the catalyst prepared in the same manner as in Example 2. 0.01 gram of bismuth oxide as a soluble bismuth compound was dissolved in 19 kg of an equimolar mixture of toluene and acetic acid (bismuth weight ratio: 5×10^{-7} in terms of bismuth metal in the liquid mixture).

[0155] To the reaction tube packed with the catalyst, were fed the liquid mixture of toluene and acetic acid containing bismuth oxide dissolved therein (3.65 g/min), oxygen (23.3 NmL/min), and nitrogen (396 NmL/min) at a reaction temperature of 170°C at a reaction pressure of 1.5 MPa (14 kg/cm^{2}G) to conduct the reaction.

[0156] The space time yield (STY) of benzyl acetate was 286 g/h/L at the reaction time of 3 hours, and this STY was maintained for 300 hours without drop. During the above reaction, palladium was not detected in the reaction liquid mixture. The results are shown in Table 7.

Example 20

[0157] The reaction and the analysis were conducted in the same manner as in Example 19 except that the amount of the bismuth used was 0.001 g (bismuth weight ratio: 5×10^{-8} in terms of bismuth metal in the liquid mixture). The results are shown collectively in Table 7.

Example 21

[0158] The reaction and the analysis were conducted in the same manner as in Example 19 except that 0.02 g of bismuth nitrate pentahydrate was used as the soluble bismuth compound (bithmuth weight ratio: 5×10^{-7} in terms of bismuth metal in the liquid mixture). The results are shown collectively in Table 7.

Example 22

[0159] Into a SUS316 reaction tube of inside diameter of 28 mm, was packed 10 cc of the catalyst prepared in the same manner as in Example 2.

[0160] 0.13 gram of bismuth oxyacetate as a soluble bismuth compound was dissolved in 19 kg of an equimolar mixture of toluene and acetic acid (bismuth weight ratio: 5×10^{-6} in terms of bismuth metal in the liquid mixture).

[0161] To the reaction tube packed with the catalyst, were fed the liquid mixture of toluene and acetic acid containing bismuth oxyacetate dissolved therein (3.65 g/min), oxygen (47 NmL/min), and nitrogen (372 NmL/min) at a reaction temperature of 170°C at a reaction pressure of 1.5 MPa (14 kg/cm^{2}G) to conduct the reaction.

[0162] The reaction mixture was separated into a gas phase and a liquid phase, and the gas phase and the liquid phase were respectively analyzed by gas chromatography. The results are shown in Table 7 collectively.

Table 1

2θ (°)	Peak intensity ratio*
38.5 ± 0.3	100
44.8 ± 0.3	35 ± 20
65.4 ± 0.3	20 ± 10
78.6 ± 0.3	20 ± 10

CuKα, 40 kV, 200 mA
* Relative intensity to the main peak taken as 100

Table 3

	STY (g/h/L)	Selectivity (%)	Half-life (h)	Pd elution rate (µg/h)	CO Adsorption (cc/g)
Example					
2	165	98	1000	3	0.00
Comparative Example					
1	226	98	165	14	0.00
2	230	97	165	14	0.00
3	150	98	200	10	0.00
4	78	98	50	10	0.03
5	121	94	24	100	1.60
6	0	0	--	--	0.00

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Table 4

	Catalyst (cc)	Reaction temperature (°C)	Reaction pressure (MPa) ((kg/cm²G))	Feed rate	Oxygen partial pressure(MPa) ((kg/cm²))	STY (g/h/L)	Selectivity (%)	Pd elution rate (μg/h)
Example 3	10	170	1.5(14)	Toluene 2.2 g/m Acetic acid 1.4 g/m Oxygen 23.2 NmL/min Nitrogen 396 NmL/min	0.06(0.6)	313	98	Not detected
Comparative example 7	10	170	1.5(14)	Toluene 2.2 g/m Acetic acid 1.4 g/m Oxygen 23.2 NmL/min Nitrogen 396 NmL/min	0.06(0.6)	160	79	184
Example 4	10	170	1.5(14)	Toluene 2.2 g/m Acetic acid 1.4 g/m Oxygen 38.5 NmL/min Nitrogen 381 NmL/min	0.1(1.0)	441	95	3
Example 5	10	170	1.5(14)	Toluene 2.2 g/m Acetic acid 1.4 g/m Oxygen 58.3 NmL/min Nitrogen 361 NmL/min	0.15(1.5)	566	94	33
Example 6	10	170	1.5(14)	Toluene 2.8 g/m Acetic acid 1.8 g/m Oxygen 58.3 NmL/min Nitrogen 990 NmL/min	0.06(0.6)	366	95	Not detected
Example 7	10	170	1.5(14)	Toluene 2.2 g/m Acetic acid 1.4 g/m Oxygen 87.5 NmL/min Nitrogen 332 NmL/min	0.22(2.25)	752	94	230
Example 7	10	170	1.5(14)	Toluene 2.2 g/m Acetic acid 1.4 g/m Oxygen 117 NmL/min Nitrogen 303 NmL/min	0.3(3.0)	837	95	570

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Table 5

	Catalyst (cc)	Reaction temperature (°C)	Reaction pressure MPa ((kg/cm²G))	Feed rate	Oxygen feed (mol/L/h)	STY (g/h/L)	Selectivity (%)	Activity half life (h)
Example 9	10	170	4.4(44)	Toluene 0.14 g/m Acetic acid 0.1 g/m Oxygen 2.7 NmL/min Nitrogen 209 NmL/min	0.7	83	95	>10000
Example 10	10	170	4.4(44)	Toluene 0.14 g/m Acetic acid 0.1 g/m Oxygen 7.8 NmL/min Nitrogen 204 NmL/min	2.1	185	95	5000
Example 11	10	170	4.4(44)	Toluene 0.14 g/m Acetic acid 0.1 g/m Oxygen 15.6 NmL/min Nitrogen 196 NmL/min	4.2	275	95	2000
Example 12	10	170	1.5(14)	Toluene 0.3 g/m Acetic acid 0.2 g/m Oxygen 5.8 NmL/min Nitrogen 51 NmL/min	1.6	201	98	>10000
Example 13	10	170	4.4(44)	Toluene 0.14 g/m Acetic acid 0.1 g/m Oxygen 20.7 NmL/min Nitrogen 191 NmL/min	5.5	283	95	1000
Example 14	10	170	4.4(44)	Toluene 0.14 g/m Acetic acid 0.1 g/m Oxygen 1.5 NmL/min Nitrogen 210 NmL/min	0.4	40	95	>10000

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Table 6

	Acetic acid/ toluene (Mole ratio)	STY (g/h/L)	Pd elution
Example 3	1	313	Not detected
Example 15	0.25	212	Not detected
Example 16	4	304	Not detected
Example 17	0.1	125	Not detected
Example 18	49	130	Not detected

Table 7

	Soluble bismuth compound	Amount of bismuth in liquid mixture*	STY (g/h/L)	Deterioration in STY **	Pd elution
Example 19	Bismuth oxide	5×10^{-7}	286	None	Not detected
Example 20	Bismuth oxide	5×10^{-8}	262	None	Not detected
Example 21	Bismuth nitrate pentahydrate	5×10^{-7}	308	None	Not detected
Example 22	Bismuth oxyacetate	5×10^{-6}	463	None	Not detected

* (Weight of bismuth as metal)/(Weight of toluene plus acetic acid)
** Deterioration in STY in 300 hours of reaction relative to initial STY

Claims

1. A process for producing benzyl acetate by oxyacetoxylation of toluene with acetic acid and oxygen which may be diluted with an inert gas such as nitrogen in a liquid phase in the presence of oxyacetoxylation-active catalyst, comprising steps of feeding toluene, acetic acid, and oxygen to an oxyacetoxylation reactor to cause reaction and to obtain an effluent from the reactor; introducing the effluent from the reactor to a gas-liquid separator to separate a gas phase mainly composed of oxygen and nitrogen and a liquid phase mainly composed of toluene, acetic acid, and benzyl acetate; introducing the liquid phase discharged from the gas-liquid separator to a starting material recovery column to separate the liquid phase by distillation into a column top distillate mainly composed of toluene and acetic acid and a column bottom liquid mainly composed of benzyl acetate; recycling the column top distillate from the starting material recovery column to the oxyacetoxylation reactor; introducing the column bottom liquid of the starting material recovery column to a low-boiler removal column to separate the column bottom liquid by distillation into a column top fraction mainly composed of benzaldehyde and a column bottom fraction mainly composed of benzyl acetate; introducing the column bottom fraction of the low-boiler removal column to a high-boiler removal column for distillation to obtain benzyl acetate from the column top thereof.

2. The process for producing benzyl acetate according to claim 1, wherein the oxygen fed to the oxyacetoxylation reactor is air, and the reactor is packed with an oxyacetoxylation active catalyst as a fixed bed.

3. The process according to claim 1 or 2, wherein the gas phase taken out from the gas-liquid separator is introduced to a condenser to separate the gas phase into a second liquid phase composed mainly of toluene, acetic acid, water, and benzyl acetate, and a second gas phase composed mainly of oxygen and nitrogen, and at least a part of the second liquid phase is fed to the starting material recovery column, and at least a part of the second gas phase is recycled to the oxyacetoxylation reactor.

4. The process according to claim 3, wherein the liquid phase removed from the condenser is introduced to a water removal column to remove most of the water by distillation, and is subsequently recycled to the oxyacetoxylation reactor.

5. A process for producing benzyl acetate by oxyacetoxylation of toluene with acetic acid and oxygen in a liquid phase in the presence of oxyacetoxylation-active catalyst, the oxyacetoxylation-active catalyst being a catalyst comprising an alloy of palladium and bismuth in a palladium/bismuth ratio ranging from 2.5 to 3.5 (atomic ratio) supported on silica.

6. The process according to claim 5, wherein the palladium supported on silica is substantially in a state of an alloy composed of palladium and bismuth.

7. The process according to claim 5 or 6, wherein the alloy composed of palladium and bismuth exhibits X-ray diffraction pattern below.

2θ (°)	Peak intensity ratio*
38.5 ± 0.3	100
44.8 ± 0.3	35 ± 20
65.4 ± 0.3	20 ± 10
78.6 ± 0.3	20 ± 10

CuKα, 40 kV, 200 mA

* Relative intensity to the main peak taken as 100

8. The process according to any of claims 5 to 7, wherein the catalyst is prepared by simultaneous impregnation of source material salts of palladium and bismuth into silica.

9. The process according to any of claims 5 to 8, wherein the catalyst is prepared by use of source material salts of palladium and bismuth in a palladium/bismuth ratio ranging from 2.5 to 3.5 (atomic ratio).

10. The process according to any of claims 5 to 9, wherein the partial pressure of the oxygen in the gas phase in the reactor is in the range of from 0.01 to 0.2 MPa (0.1 to 2 kg/cm^2).

11. The process according to any of claims 5 to 10, wherein the oxygen is fed at a rate ranging from 0.5 to 4.5 mol/h per liter of the catalyst.

12. The process according to any of claims 5 to 11, wherein the reaction is conducted at a mixing ratio of acetic acid to toluene ranging from 0.2 to 40 (mole ratio).

13. The process according to any of claims 5 to 12, wherein the reaction is conducted with a soluble bismuth compound dissolved in toluene and/or acetic acid.

14. The process according to claim 13, wherein the soluble bismuth compound is used in an amount:

$$1 \times 10^{-9} \leq \frac{\text{Weight of bismuth as metal}}{\text{Weight of toluene + acetic acid}} \leq 1 \times 10^{-5}$$

Patentansprüche

1. Verfahren zur Herstellung von Benzylacetat durch Oxyacetoxylierung von Toluol mit Essigsäure und Sauerstoff, der mit einem Inertgas, wie z.B. Stickstoff, verdünnt sein kann, in einer Flüssigphase in Gegenwart eines oxyacetoxylierungsaktiven Katalysators, umfassend die Schritte: Zuführen von Toluol, Essigsäure und Sauerstoff zu einem Oxyacetoxylierungsreaktor, um eine Umsetzung zu bewirken und ein ausfließendes Medium aus dem Reaktor zu erhalten; Einbringen des ausfließenden Mediums aus dem Reaktor in einen Gas-Flüssigkeit-Separator, um eine Gasphase, die hauptsächlich aus Sauerstoff und Stickstoff zusammengesetzt ist, und eine Flüssigphase, die hauptsächlich aus Toluol, Essigsäure und Benzylacetat zusammengesetzt ist, zu trennen; Einbringen der aus dem Gas-Flüssigkeit-Separator entnommenen Flüssigphase in eine Säule zur Gewinnung von Ausgangsmaterial, um die Flüssigphase durch Destillation in ein Säulenkopfdestillat, das hauptsächlich aus Toluol und Essigsäure zusammengesetzt ist, und eine Säulenbodenflüssigkeit, die hauptsächlich aus Benzylacetat zusammengesetzt ist, zu trennen; Rückführen des Säulenkopfdestillats aus der Säule zur Gewinnung von Ausgangsmaterial in den Oxyacetoxylierungsreaktor; Einbringen der Säulenbodenflüssigkeit aus der Säule zur Gewinnung von Ausgangsmaterial in eine Säule zur Entfernung niedrigsiedender Stoffe, um die Säulenbodenflüssigkeit durch Destillation in eine Säulenkopffraktion, die hauptsächlich aus Benzaldehyd zusammengesetzt ist, und eine Säulenbodenfraktion, die hauptsächlich aus Benzylacetat zusammengesetzt ist, zu trennen; Einbringen der Säulenbodenfraktion der Säule zur Entfernung niedrigsiedender Stoffe in eine Säule zur Entfernung höhersiedender Stoffe zur Destillation, um Benzylacetat aus dem Säulenkopf zu erhalten.

2. Verfahren zur Herstellung von Benzylacetat nach Anspruch 1, wobei der dem Oxyacetoxylierungsreaktor zugeführte Sauerstoff Luft ist und der Reaktor mit einem oxyacetoxylierungsaktiven Katalysator als Festbett gefüllt ist.

3. Verfahren nach Anspruch 1 oder 2, wobei die aus dem Gas-Flüssigkeit-Separator entnommene Gasphase in einen Kondensator eingebracht wird, um die Gasphase in eine zweite Flüssigphase, die hauptsächlich aus Toluol, Essigsäure, Wasser und Benzylacetat zusammengesetzt ist, und eine zweite Gasphase, die hauptsächlich aus Sauerstoff und Stickstoff zusammengesetzt ist, zu trennen, und zumindest ein Teil der zweiten Flüssigphase der Säule zur Gewinnung von Ausgangsmaterial zugeführt wird, und zumindest ein Teil der zweiten Gasphase in den Oxyacetoxylierungsreaktor rückgeführt wird.

4. Verfahren nach Anspruch 3, wobei die aus dem Kondensator entnommene Flüssigphase in eine Säule zur Entfernung von Wasser eingebracht wird, um den Großteil des Wassers durch Destillation zu entfernen, und anschließend in den Oxyacetoxylierungsreaktor rückgeführt wird.

5. Verfahren zur Herstellung von Benzylacetat durch Oxyacetoxylierung von Toluol mit Essigsäure und Sauerstoff in einer Flüssigphase in Gegenwart eines oxyacetoxylierungsaktiven Katalysators, wobei der oxyacetoxylierungsaktive Katalysator ein Katalysator ist, der eine Legierung von Palladium und Wismut in einem Palladium/Wismut-Verhältnis im Bereich von 2,5 bis 3,5 (Atomverhältnis) auf einem Siliciumdioxidträger umfaßt.

6. Verfahren nach Anspruch 5, wobei das Palladium auf einem Siliciumdioxidträger im wesentlichen im Zustand einer aus Palladium und Wismut zusammengesetzten Legierung vorliegt.

7. Verfahren nach Anspruch 5 oder 6, wobei die aus Palladium und Wismut zusammengesetzte Legierung das nach-

stehende Röntgenbeugungsmuster aufweist.

2θ (°)	Peak-Intensitätsverhältnis*
38,5 ± 0,3	100
44,8 ± 0,3	35 ± 20
65,4 ± 0,3	20 ± 10
78,6 ± 0,3	20 ± 10

CuKα, 40 kV, 200 mA
* relative Intensität bezogen auf den Haupt-Peak als Wert 100

8. Verfahren nach einem der Ansprüche 5 bis 7, wobei der Katalysator durch gleichzeitiges Imprägnieren von Siliciumdioxid mit den Ausgangsmaterial-Salzen von Palladium und Wismut hergestellt wird.

9. Verfahren nach einem der Ansprüche 5 bis 8, wobei der Katalysator durch Verwendung von Ausgangsmaterial-Salzen von Palladium und Wismut in einem Palladium/Wismut-Verhältnis im Bereich von 2,5 bis 3,5 (Atomverhältnis) hergestellt wird.

10. Verfahren nach einem der Ansprüche 5 bis 9, wobei der Sauerstoffpartialdruck in der Gasphase in dem Reaktor im Bereich von 0,01 bis 0,2 MPa (0,1 bis 2 kg/cm^2) liegt.

11. Verfahren nach einem der Ansprüche 5 bis 10, wobei der Sauerstoff mit einer Rate im Bereich von 0,5 bis 4,5 Mol/h pro Liter des Katalysators zugeführt wird.

12. Verfahren nach einem der Ansprüche 5 bis 11, wobei die Umsetzung bei einem Mischungsverhältnis von Essigsäure zu Toluol im Bereich von 0,2 bis 40 (Molverhältnis) durchgeführt wird.

13. Verfahren nach einem der Ansprüche 5 bis 12, wobei die Umsetzung mit einer in Toluol und/oder Essigsäure gelösten löslichen Wismutverbindung durchgeführt wird.

14. Verfahren nach Anspruch 13, wobei die lösliche Wismutverbindung in einer Menge verwendet wird:

$$1 \times 10^{-9} \leq \frac{\text{Gewicht von Wismut als Metall}}{\text{Gewicht von Toluol + Essigsäure}} \leq 1 \times 10^{-5}$$

Revendications

1. Procédé pour préparer de l'acétate de benzyle par oxyacétoxylation du toluène avec de l'acide acétique et de l'oxygène qui peut être dilué avec un gaz inerte comme de l'azote en phase liquide en présence d'un catalyseur actif pour une oxyacétoxylation, comprenant les étapes consistant à : envoyer le toluène, l'acide acétique et l'oxygène dans un réacteur d'oxyacétoxylation pour provoquer une réaction et pour obtenir un effluent depuis le réacteur; introduire l'effluent depuis le réacteur dans un séparateur de gaz-liquide pour séparer une phase gazeuse composée principalement d'oxygène et d'azote et une phase liquide composée principalement de toluène, d'acide acétique, et d'acétate de benzyle; introduire la phase liquide déchargée depuis le séparateur de gaz-liquide dans une colonne de récupération des produits de départ pour séparer la phase liquide par distillation en un produit de distillation de haut de colonne principalement composé de toluène et d'acide acétique et un liquide de fond de colonne principalement composé d'acétate de benzyle; recycler le produit de distillation de haut de colonne depuis la colonne de récupération des produits de départ vers le réacteur d'oxyacétoxylation; introduire le liquide de fond de colonne de la colonne de récupération des produits de départ dans une colonne d'enlèvement pour les bas points d'ébullition pour séparer le liquide de fond de colonne par distillation en une fraction de haut de colonne principalement composée de benzaldéhyde et une fraction de fond de colonne principalement composée d'acétate de benzyle; introduire la fraction de fond de colonne de la colonne d'enlèvement pour les bas points d'ébullition dans une colonne d'enlèvement pour les hauts points d'ébullition pour une distillation pour obtenir de l'acétate de benzyle à partir du haut de cette colonne.

2. Procédé pour préparer de l'acétate de benzyle selon la revendication 1, dans lequel l'oxygène envoyé dans le réacteur d'oxyacétoxylation est de l'air, et le réacteur est garni avec un catalyseur actif pour une oxyacétoxylation

sous la forme d'un lit fixe.

3. Procédé selon la revendication 1 ou 2, dans lequel la phase gazeuse enlevée du séparateur de gaz-liquide est introduite dans un condenseur pour séparer la phase gazeuse en une seconde phase liquide principalement composée de toluène, d'acide acétique, d'eau et d'acétate de benzyle, et une seconde phase gazeuse principalement composée d'oxygène et d'azote, et au moins une partie de la seconde phase liquide est envoyée dans la colonne de récupération des produits de départ, et au moins une partie de la seconde phase gazeuse est recyclée dans le réacteur d'oxyacétoxylation.

4. Procédé selon la revendication 3, dans lequel la phase liquide enlevée du condenseur est introduite dans une colonne d'enlèvement de l'eau pour enlever la majorité de l'eau par distillation, et est ensuite recyclée dans le réacteur d'oxyacétoxylation.

5. Procédé pour préparer de l'acétate de benzyle par oxyacétoxylation du toluène avec de l'acide acétique et de l'oxygène en phase liquide en présence d'un catalyseur actif pour une oxyacétoxylation, le catalyseur actif pour une oxyacétoxylation étant un catalyseur comprenant un alliage de palladium et de bismuth dans un rapport palladium/bismuth allant de 2,5 à 3,5 (rapport atomique) fixé sur un support de silice.

6. Procédé selon la revendication 5, dans lequel le palladium fixé sur un support de silice est essentiellement dans un état d'un alliage composé de palladium et de bismuth.

7. Procédé selon la revendication 5 ou 6, dans lequel l'alliage composé de palladium et de bismuth présente le motif de diffraction des rayons X ci-dessous.

2θ(°)	Rapport d'intensité des pics*
38,5 ± 0,3	100
44,8 ± 0,3	35 ± 20
65,4 ± 0,3	20 ± 10
78,6 ± 0,3	20 ± 10

CuKα, 40 kV, 200 mA
* Intensité relative par rapport au pic principal pris comme 100

8. Procédé selon l'une quelconque des revendications 5 à 7, dans lequel le catalyseur est préparé par imprégnation simultanée de sels de palladium et de bismuth comme matières sources dans de la silice.

9. Procédé selon l'une quelconque des revendication 5 à 8, dans lequel le catalyseur est préparé en utilisant des sels de palladium et de bismuth comme matières sources dans un rapport palladium/bismuth allant de 2,5 à 3,5 (rapport atomique).

10. Procédé selon l'une quelconque des revendications 5 à 9, dans lequel la pression partielle de l'oxygène dans la phase gazeuse dans le réacteur se situe dans la gamme de 0,01 à 0,2 MPa (0,1 à 2 kg/cm^2).

11. Procédé selon l'une quelconque des revendications 5 à 10, dans lequel l'oxygène est envoyé à un débit allant de 0,5 à 4,5 moles/heure par litre du catalyseur.

12. Procédé selon l'une quelconque des revendications 5 à 11, dans lequel la réaction est effectuée à un rapport de mélange de l'acide acétique sur le toluène allant de 0,2 à 40 (rapport molaire).

13. Procédé selon l'une quelconque des revendications 5 à 12, dans lequel la réaction est effectuée avec un composé de bismuth soluble dissous dans du toluène et/ou de l'acide acétique.

14. Procédé selon la revendication 13, dans lequel le composé de bismuth soluble est utilisé dans une quantité :

$$1 \times 10^{-9} \leq \frac{\text{Poids de bismuth en tant que métal}}{\text{Poids du toluène + acide acétique}} \leq 1 \times 10^{-5}$$

FIG. 1

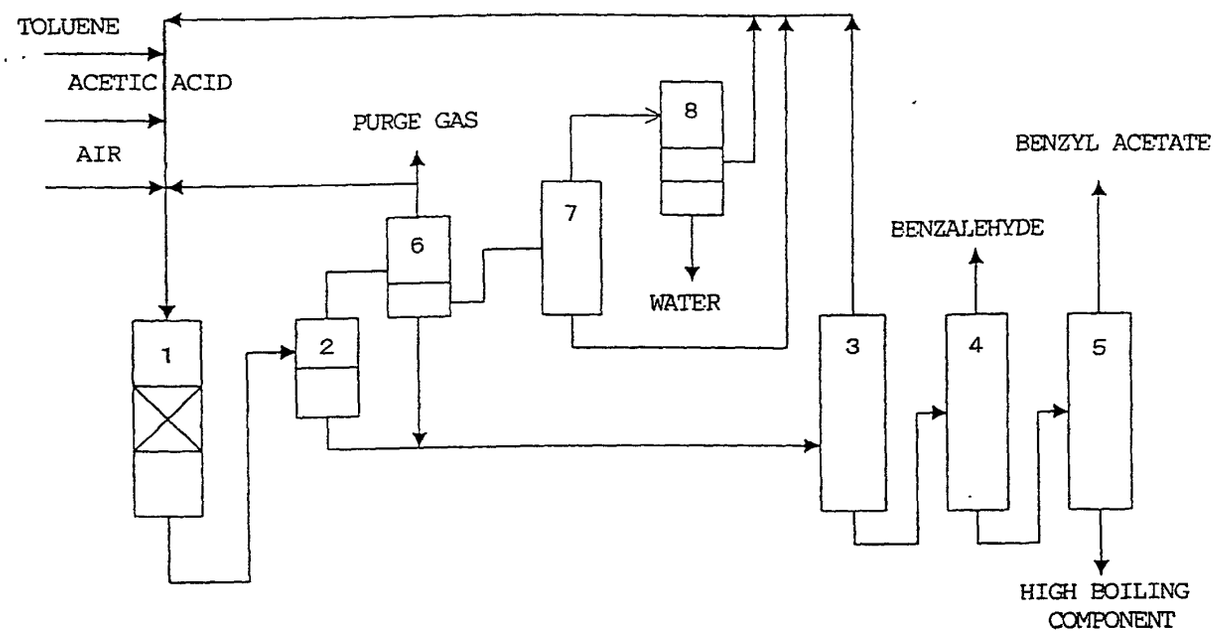
TOLUENE
ACETIC ACID
AIR
PURGE GAS
WATER
BENZALEHYDE
BENZYL ACETATE
HIGH BOILING COMPONENT
1
2
3
4
5
6
7
8

FIG. 2

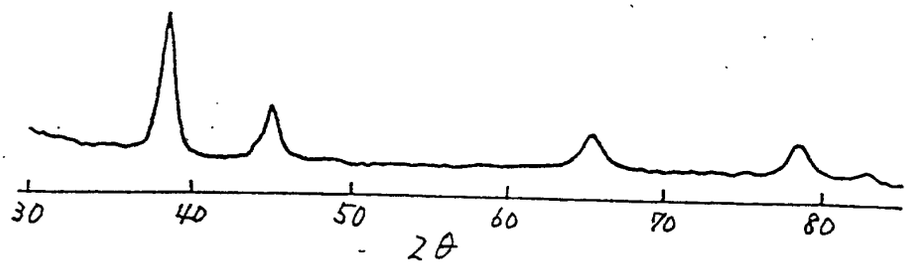

FIG. 3

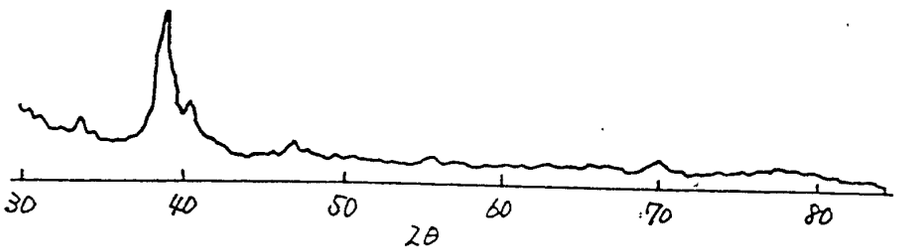

FIG. 4

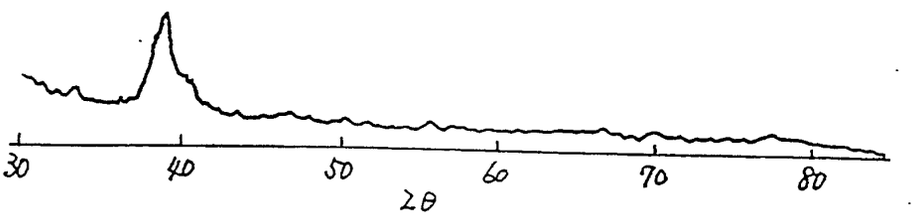

FIG. 5

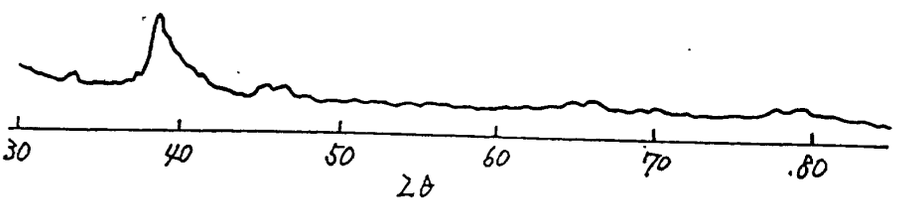

FIG. 6